(d) Gas Species Measurement

by

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What gas species, besides oxygen, might we wish to measure? Primarily, we are interested in either those which can serve as combustion diagnostics (e.g., H_2O, CO_2, total unburned hydrocarbons) or those which are of interest from a toxicity point of view (e.g., CO, HCl, HBR, HF, HCN, NO_2). The instrumentation for making gas species measurements was already discussed in Chapter 3 above. Here, we wish to consider how the data might be used, once obtained.

If one examines old fire testing literature, one typically finds gas concentrations quoted in either percent or parts-per-million (ppm) units, both usually being taken on a volume basis. These numbers, unfortunately have almost no generality, and therefore precious little utility. If one knows that, during a certain test fire, the HCN concentration 1 m below the ceiling and 0.5 m outside the door of the burn room was 100 ppm, there is very little that can be done with that data. If we know that a human being's nose will be located at exactly that level, perhaps the information can help us in assessing the survivability. Otherwise, the information is not valuable because it does not, in any sense, represent a **property of the test material or product**. While realizing that most fire properties are not as invariable as, say, the density of iron at 25 °C, we nonetheless recognize the importance of obtaining material properties. They have value because we expect to be able to change the fire scenario, but re-use the material properties by finding them to be equally applicable to the new scenario. We already saw an example of this earlier, where progress in fire testing was tied to the ability to go beyond temperatures (which are not a material property) and heat release rate (which is, given certain constraints). In this Section, we will consider how results for gas species measurements might be expressed and evaluated so as to possess this 'portability.'

DATA FROM BENCH-SCALE TESTS

In a bench-scale test, we will assume concomitant load cell data to be available. Such is true, for instance, of the Cone Calorimeter, although it was not necessarily true for early test apparatuses. With load cell information available, the simplest measure is the **yield**. The yield of any species x is defined as

$$f_x = \frac{(kg\ x\ produced)}{(kg\ specimen\ mass\ lost)}$$

and can be computed as specified in Chapter 3. This definition of yield does not specify a *time* interval. In general, we may be interested in two possibilities: (1) the average yield, over the entire duration of burning; or (2) a time-varying yield, computed at each instant as a function of time. For product evaluation, it has generally been found adequate to report just the average yield values. For the development chemist, however, the time-varying data can provide significant additional information.

Looking now from the manufacturer's point of view, it is clear that he should not simply report yields as an indicator of relative product merit. To perform some hazard analysis, even if it be as crude as rank-ordering products, it is necessary to include a *rate factor*, and thereby derive a **production rate** or, instead, to simply evaluate the **production**.

How to choose between production and production rate?

Whether products should be compared, rank-ordered, etc., according to their production rate or according to the production will depend on the hazard that is to be guarded against. The (total) production value is more important if the occupant at risk is far away from fire, and is affected mainly by the cumulated values. By contrast, an occupant close to the fire may perish before the combustible is even fully burned up, and is much more likely to be concerned about production rate.

To illustrate by means of a concrete example, let us assume that the hazard in question is the gas hydrogen fluoride (HF), evolved from certain fluorinated polymers. The specimen is being burned in the Cone Calorimeter and has the standard exposed surface area of 0.01 m^2. The (total) production of HF will be evaluated as (kg HF)/(m^2 specimen area); thus the units will be $kg \cdot m^{-2}$. The production rate must have the units of (kg HF)/($s \cdot m^2$ specimen area), or $kg\ s^{-1} m^{-2}$.

Production rate

The production rate can be computed directly at each instant of time by evaluating (kg HF)/($s \cdot m^2$ specimen area) at each instant that data are collected. Alternatively, it can

be viewed as comprised of two factors, the yield of HF and the mass loss rate of the specimen. It is clear that appropriate time periods need to be specified. For many materials, the yield may vary only insignificantly over the duration of the test. Mass loss rates will never be completely constant for a test, however. The time period during which to perform the evaluation would, in principle, be determined by a complete hazard analysis of the given problem. A manufacturer compiling a data sheet on his product, however, does not have such a luxury—he may not know what use the product will be put to. Thus, there is some advantage in suggesting a generic procedure here. In such a simplest case, assume that the yield has no significant variations over time, and select the test-average yield for HF. For $\dot{m}''$ it has been found convenient to define a '90 - 10' value, which covers the entire burning period of the specimen, except for the first and the last 10% of mass lost. (It is not sensible to define a '100 - 0' measure, since mass loss rates may indefinitely trail off to zero, especially at the tail end of a test.) We define this '90 - 10' mass loss rate as MLR:

$$MLR = \frac{m_{90} - m_{10}}{t_{10} - t_{90}}$$

where

m_{90} = mass loss equal to 90% of consumed mass (kg/m^2)
m_{10} = mass loss equal to 10% of consumed mass (kg/m^2)
t_{90} = time at which m_{90} occurs (s)
t_{10} = time at which m_{10} occurs (s)

It has been found that, thus defined, the MLR is usually easy and unequivocal to compute [1]. Then, the production rate can be computed as:

$$production\ rate = yield \times MLR$$

and we note that the units will be (kg HF)/($s \cdot m^2$). This must be accompanied by a statement describing that it was the '90 - 10' period that was used.

Production

The production—of any combustion product—is not a rate; it is the total evolution of that product. For a bench-scale test, however, the specimen is restricted to a small area; thus, we are not measuring its true production. To get at a material property, one which might successfully transfer to the full scale, it is necessary to normalize by the exposed specimen area. Thus, the units in our example would be (kg HF)/(m^2 specimen area), or $kg \cdot m^{-2}$. Computationally, this is a summation: the total kg of HF evolved is added up for the whole test, then divided by the exposed specimen area.

The production, thus determined, is also appropriately listed by a manufacturer in his data sheets.

DATA FROM FULL-SCALE TESTS

Full-scale tests differ from bench-scale ones in the essential trait that the specimen area here is actual; there is no need to normalize results by exposed surface area. Production rates and (total) production values can be quoted directly, as an input to hand or computer methods for computing fire hazard.

When we wish to compare full-scale against bench-scale data, the question becomes: What units to compare? One important consideration is that in the full-scale test the actual burning area is often unknown. Since flame spread and burnout can both be expected to occur, the burning area is not the same as the exposed specimen area (unlike in the bench-scale HRR test, where the specimen face is ignited all at once). Thus, measures involving m^2 in the denominator are not likely to be appropriate candidates for correlation. Instead, it can be seen that this is the proper role for the *yield*. The (kg product)/(kg specimen burned) is, to a first approximation, independent of the specimen area which is burning. Thus, when comparing bench-scale and full-scale results for gas species, the basis of comparison is the yield. Extensive examples are given in [2] and [3].

ADDITIONAL CONSIDERATIONS

Smoke and soot measurements

When soot is measured gravimetrically, by weighing what is collected on filter paper, the basic measurement is (kg soot). The analysis proceeds exactly as for data where (kg gas) was the variable recorded.

When smoke is measured optically, by the attenuation of a light beam, the raw data is the light attenuation (dimensionless fraction) over a given beam length (m). This is recorded as an *extinction coefficient*, k (m^{-1}), as a function of time. By multiplying by the actual, volumetric flow rate (m^3/s), we get *extinction area rate*, (m^2/s). This variable is, perhaps, unfamiliar because it is typically only an intermediate calculation quantity. More commonly, the *extinction area*, σ_f (m^2/kg), is reported. This is the 'yield' of smoke; it can be treated exactly the same way as gas yields and is different only in that the 'product' in question is expressed as an area, not as a mass. The mass in the denominator (the kg of specimen mass lost) has the identical role in this case.

Same as for product gases, the yield is the appropriate quantity to use in comparing bench-scale to full-scale data, but is never the proper ranking scale for products. By exact analogy to the case of the gases, we can define a *smoke production rate* (m^2 smoke/s·m^2 specimen area). Perhaps somewhat confusingly, the units of m^2 cancel out top and bottom, leaving (s^{-1}). It may be more clear to retain the m^2 on both parts of the fraction to emphasize that these are m^2 of different things. This is not too different from writing gas yields as (kg/kg), instead of as (—).

Similarly, the total smoke produced from a specimen, normalized by the exposed specimen area, is the *smoke production*, and has units of (m^2/m^2).

For full-scale tests, smoke production rate is (m^2/s), while (total) smoke production is (m^2).

Heat-based variables

For manufacturers it is often of primary importance to report HRR values, either peaks, or certain time averages, depending on what may be of importance to the potential application. By contrast, mass loss rates are rarely tabulated or compared. Thus, in the commercial sector there has been an interest in deriving production rates where a $\dot{q}''$ factor, rather than the $\dot{m}''$ factor might be used. It can be seen that

$$\frac{yield\ (kg/kg)}{\Delta h_c\ (MJ/kg)} \times \dot{q}''\ (kW/m^2) = production\ rate\ (kg{\cdot}s^{-1}{\cdot}m^{-2})$$

Thus, for the purposes of multiplying by $\dot{q}''$, we tabulate (yield x)/Δh_c, instead of (yield x).

The units of this combined expression, in the example case of HF computation, would be (kg HF)/kJ; thus, we might term this the 'HF/heat ratio.'

REFERENCES

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